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RECOVERY AND UTILIZATION OF NATURAL APPLE FLAVORS

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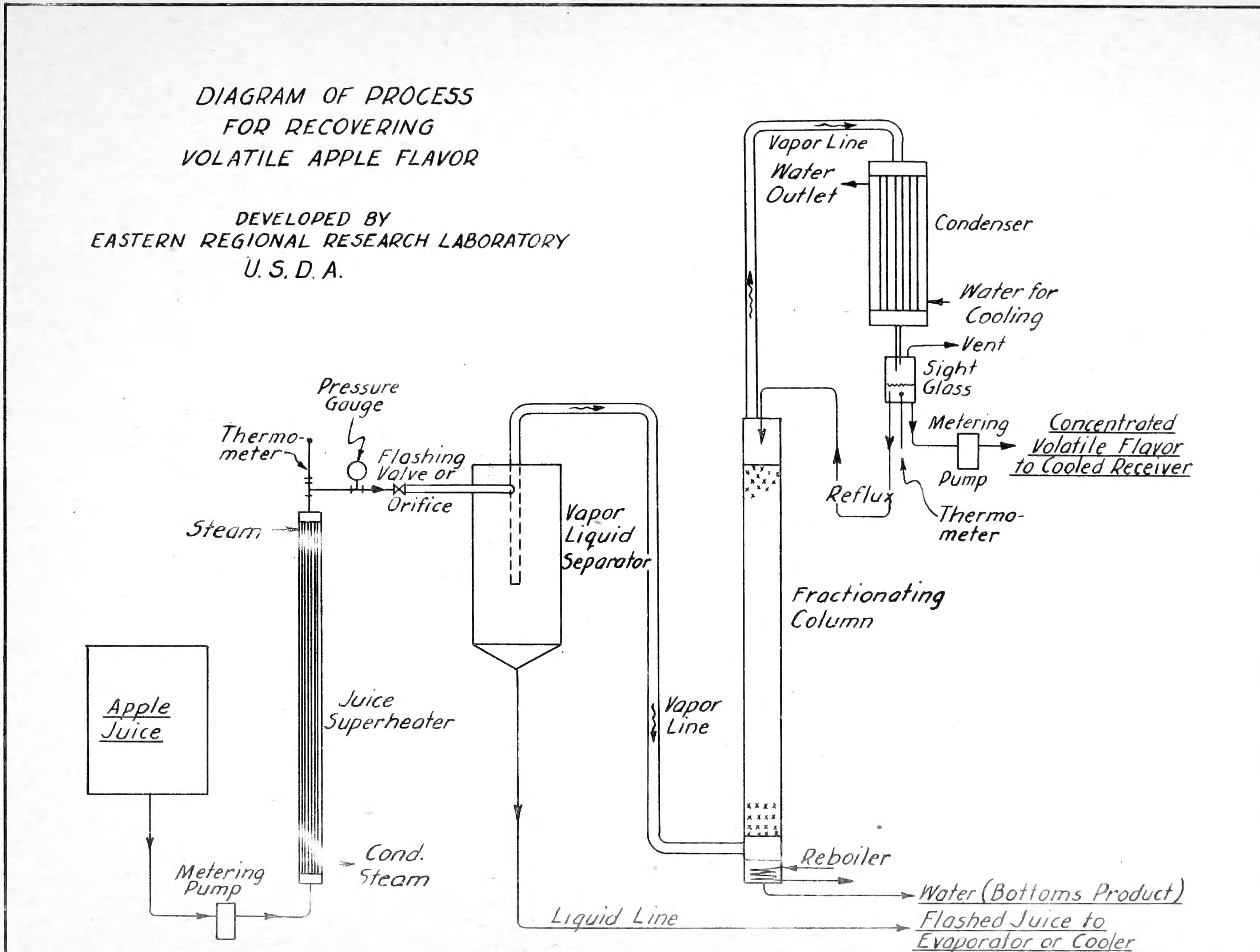
DIAGRAM OF PROCESS
FOR RECOVERING
VOLATILE APPLE FLAVOR
DEVELOPED BY
EASTERN REGIONAL RESEARCH LABORATORY
U. S. D. A.
Apple Juice
Metering Pump
Steam
Thermo-meter
Pressure Gauge
Flashing Valve or Orifice
Juice Superheater
Cond. Steam
Vapor Liquid Separator
Vapor Line
Liquid Line
Fractionating Column
Reboiler
Vapor Line
Water Outlet
Condenser
Water for Cooling
Vent
Sight Glass
Metering Pump
Reflux
Thermo-meter
Concentrated Volatile Flavor to Cooled Receiver
Water (Bottoms Product)
Flashed Juice to Evaporator or Cooler

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Recovery and Utilization of Natural Apple Flavors

By Howard P. Milleville[1] and Roderick K. Eskew[2]

INTRODUCTION

In the preparation of bland apple sirup[3] and commercial apple concentrates[4], the volatile flavoring constituents of the fresh juice, which give the natural bouquet, are completely lost. The numerous attempts made in this and other countries during the past 20 years to recover these flavors have never been completely successful, because either some of the more volatile components were lost or in the course of recovery the initial fresh flavor was inadvertently altered. This circular describes a comparatively simple method for completely recovering the natural flavor of fresh apples in an unaltered form and suggests commercial uses for such a product.

The full possibilities of the process have not yet been evaluated, but since the basic principles are well developed and the chemical engineering aspects of the problem are relatively simple it seems desirable to make this information available now.

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The authors are indebted to George W. Macpherson Phillips for technical advice and many valuable suggestions in the preparation of the manuscript and to Edward L. Griffin for his excellent assistance in carrying out the experimental work.

3. "BLAND APPLE SIRUP," by H. H. Mottern and R. H. Morris, 3rd. Mimeograph circular AIC-37

4. By "apple concentrate" is meant a material prepared by vacuum evaporation of apple juice without any alteration of its natural acid content; "apple sirup" signifies concentrated products whose natural acid content has been reduced.

THE PRODUCT

The product is a colorless water solution of the volatile constituents of natural apple flavor concentrated from 100- to 150-fold. Even in this concentrated state, however, the actual proportion of flavoring constituents in the solution does not exceed a few tenths of one percent by weight. The odor is mildly pungent, a characteristic common to concentrated flavoring essences. No perceptible changes occur in the product during storage; apparently it will keep indefinitely.

Blending the flavor concentrate with a good grade of filtered apple juice that has been concentrated by vacuum evaporation results in a full-flavored apple juice concentrate, which when reconstituted with water, is indistinguishable in taste and aroma from fresh apple juice.

THE PROCESS

Basis of Process

In our studies, five significant facts were established:

(1) The flavor of fresh apple juice is not impaired by heating it to 320° F. in 3 seconds.

(2) A 10-percent flash vaporization is sufficient to remove all the volatile flavors; in fact, less than 10 percent may be sufficient for practical purposes.

(3) The freshness of the volatile flavor after it is separated from the juice is not affected by prolonged exposure to the boiling temperature of water, such as occurs in a fractional distillation column.

(4) At atmospheric pressure and 70° F., the volatile flavoring constituents can be recovered in the distillate in concentrations up to 150 times that in apple juice.

(5) A rectifying section of a continuous fractional distillation column with vapor feed is all that is required to effect

this concentration, a small reboiler at the base of the column being sufficient to prevent loss of flavors in the waste (bottoms product) from the rectifying column.

The process, illustrated in Figure 1, consists of the following steps: (1) superheating the juice; (2) flash vaporizing the superheated juice at atmospheric pressure; (3) mechanically separating the vapors from the unvaporized juice; and (4) fractionating the vapors to obtain a more concentrated flavor. The process has been successful on a pilot-plant scale of 10 gallons of juice per hour.

Preparing the Juice

The juice should be pressed from sound apples, because any volatile off-flavors in the juice are also recovered. Since the characteristics of the flavor, including the aroma, are dependent upon the variety of apples used, blending different varieties should be taken into consideration as a means for controlling and improving the flavor of the product. Most of the volatile flavor of apples has been shown to be located just under the skin; hence, the skin should be disintegrated as much as possible in the grating or hammer-milling operations preparatory to pressing in order to liberate the flavors. On the other hand, disintegration of the seeds results in the freeing of an apple-seed flavor resembling that of bitter almonds, which is recovered with the other flavors. Although this is not disagreeable, it is undesirable because it is not characteristic of the flavor of fresh apples.

To prevent fouling of the flavor recovery equipment the juice should be screened. It may be advantageous not to filter it at this stage, as some of the flavoring elements may be eliminated by too complete clarification.

Superheating and Flash Vaporizing the Juice

To obtain approximately 10-percent vaporization, the juice may be heated to about 320° F. under pressure, then released into an atmospheric-pressure flash chamber. A possible alternate method would be to heat and vaporize the juice simultaneously by a single passage through a continuous evaporator. The essential requirement of the process is that the juice be heated rapidly enough to avoid modifying the fresh flavor. The extreme conditions of time and temperature that can be used safely are not yet known, but it was found that heating the juice to 320° F. in 3 seconds had no effect on the flavor.

When pectin-containing solutions, such as apple juice, are heated by passing through a metallic tube held above a certain critical temperature, presumably different for different solutions, a loosely adherent gelatinous film may be deposited on the tube. This occurred in the superheater in our pilot-plant work and greatly reduced the heat transfer in a few hours. The film was quickly removed by pumping water through the tube at the same rate as that previously used for juice. Means for preventing the formation of this film are under investigation.

In the flash-vaporization system, the evaporation takes place when the pressure on the superheated juice is released. The superheat of the liquid is then transformed into latent heat of vaporization. At 320° F. the pressure required to maintain the juice in the liquid phase is 75 lbs. per sq. in. (gauge); therefore the juice must be kept at 75 lbs. per sq. in. (gauge) or more until it is flashed. In a continuous process, this requirement is achieved by means of a restriction at the end of the superheated juice line, which can be either a throttling-type valve or an orifice plate.

Separating the Vapors from the Unvaporized Juice

The flashing operation produces an intimate mixture of vapor and liquid, which must be separated. A small amount of entrained juice in the vapor can be tolerated, for the sugar and other solids which it contains will be subsequently removed in the fractionating column. Juice so entrained is lost for further processing, for it will be discarded as an extremely dilute solution in the bottoms product from the fractionating column.

Fractionating the Vapors

In the flashed vapors the volatile flavoring constituents are present in a concentration approximately 10 times that of apple juice. The relatively dilute fraction thus obtained is difficult to utilize. For instance, its addition to the sirup of 80° Brix (approximately 80 percent solids by weight) resulting from the evaporation of this apple juice would give a product of 50° Brix. This is less than that of commercial sirups, and would result in a product of poor keeping quality. The flashed vapors are therefore further concentrated in a fractionating column, as shown in Figure 1. When the flavor fraction is concentrated 100-fold and then added to 80° Brix sirup the resulting dilution is only 4.5° Brix. The fractionation is easily accomplished. In the pilot-plant studies a depth of 3-1/2 feet of porcelain Raschig rings of 3/8-inch diameter was sufficient to effect a 10-fold increase in concentration of volatile flavoring constituents, that is, to 100 times that of the apple juice.

The vapors from the column pass to a total condenser. The product is withdrawn from the condensate receiver at a rate of 1/100 to 1/150 that of the fresh juice feed rate. The remainder of the condensate is

returned through an overflow as reflux to the column. The reflux in the pilot plant studies was returned cold to eliminate the need for a reflux preheater, thus simplifying the operation of the column. A small heating coil or reboiler at the base of the column is used to strip off any volatile flavors from the waste water leaving the bottom of the column.

In the pilot plant studies, the temperature of the condensate was maintained at 70° F. At this temperature the maximum attainable concentration of volatile flavors is about 150 times that in the fresh juice, that is, 1 gallon of product contains the volatile flavor of 150 gallons of juice. Attempts to obtain higher concentrations resulted in losses; the unrecovered flavors escaped through the vent along with the noncondensable gases introduced into the system in the apple juice. Below this concentration the losses that occurred by venting these noncondensable gases (which, of course, leave the system saturated with the volatile flavors) were negligible. In one typical run, the rate at which the noncondensable gases were vented from the system was 2 percent of the apple juice-feed rate expressed on a volume basis.

Operation and Control

Operation and control of the process are rather simple. The two constant-rate liquid pumps, one on the fresh-juice feed line and the other on the product discharge line, are set at predetermined rates as desired. For instance, to obtain a 150-fold concentration of flavor, the product pump is set at 1/150 of the rate of the feed pump. For the proper operation of the flash-vaporization system, the flashing

valve or orifice is adjusted to give a pressure drop across it sufficient to prevent vaporization ahead of the orifice. Then the only variables which have to be controlled are the superheated juice temperature and the condensate temperature. Pilot plant experience has shown that if the former is held between 300° and 320° F. and the latter between 60° and 80° F., no detectable variation is noticeable in the flavor product concentrated to about 125-fold. For higher concentrations, the condensate temperature might have to be kept within the range of 60° and 70° F.

Baked-Apple Flavor

For some purposes a concentrated baked-apple flavor may be more suitable than the natural, fresh apple flavor, especially for food products that are not consumed cold. The baked flavors are developed by increasing the time or the temperature of heating the juice before removing the volatile flavor fraction. With slight modifications the same equipment used for recovery of fresh flavor could be used to produce and recover baked flavor. Baked-apple flavor is stronger than fresh apple flavor, that is, it is detectable by odor at much greater dilutions than the fresh flavor. The studies on baked-apple flavor are not yet completed.

EQUIPMENT REQUIRED

This process for the production of apple flavor would seem suitable for immediate adoption by present manufacturers of bland apple sirups and concentrates. Estimates of equipment requirements and processing costs have been made on that basis. It is assumed that steam at 120 lbs. per sq. in. (gauge) is available for the superheater. If it is not, then instead of installing a new boiler to

obtain the 120 lbs. per sq. in., a single-pass, continuous, high-speed evaporator should be considered, because in it the heating and evaporation both take place at atmospheric pressure and low-pressure steam can be used for heating. The cost of the steam for both the superheater and the continuous evaporator, except for the small amount required by the reboiler, can be considered as chargeable to the manufacture of the sirup produced from the juice, because the concentration effected by this preliminary evaporation lessens the load on the sirup evaporators.

The following equipment is required:

Metering pumps	2
Juice superheaters (one a spare)	2
Vapor-liquid separator	1
Fractionating column	1
Condenser	1
Miscellaneous piping and fittings	

Copper is a suitable material for apparatus for manufacturing apple sirup if the surface is kept bright, that is, not allowed to become oxidized by intermittent use. It should also be satisfactory for all the apparatus required for recovery of flavor except the superheater and the metering pumps. The pumps can be bronze, but for the superheater stainless steel is recommended. Apple juice at the high temperature which it reaches in the superheater may slightly attack copper and bronze and thus be contaminated.

The metering pump on the feed line should preferably be duplex or double-acting to reduce the pulsations inherent in reciprocating pumps and even then a small surge chamber may be desirable. The small

metering pump on the product line may be a single-acting pump, for the pulsations caused by it are of no consequence. This pump delivers against a low pressure, whereas the large pump on the feed line must be capable of delivering the juice at a pressure sufficient to maintain it in liquid phase up to the flashing orifice as well as to overcome the drop in pressure resulting from the flow of juice through the superheater.

On the basis of present pilot plant data, a single-tube superheater with a tube of 0.334-inch inside diameter ($\frac{1}{2}$ inch outside diameter, #14 gauge wall) and 38 feet long and with steam at 100 to 120 lbs. per sq. in. (gauge) as the heating medium should superheat 208 gallons of apple juice per hour (5,000 gallons per 24-hour day) to 320° F. in 3 seconds. The pressure drop through such a superheater would not exceed 40 lbs. per sq. in. To maintain the juice in liquid phase, the pressure drop across the flashing orifice must be at least 75 lbs. per sq. in. With proper design this orifice pressure drop will not exceed 160 lbs. per sq. in.; hence, the overall drop in pressure on the juice line from the pump to the low-pressure side of the flashing orifice will not exceed 200 lbs. per sq. in. It is recommended that two superheaters be installed in parallel, each of sufficient capacity to operate singly, in order that cleaning and inspection can be carried on without interrupting operations. To facilitate inspection and cleaning, the superheaters should be constructed with easily removable heads.

It may be possible to substitute certain types of pasteurizers for the superheater described. The important consideration is that the time required to heat the juice in the apparatus be short enough

to avoid altering the fresh flavor of the juice.

As already mentioned, a single-pass evaporator, so designed as to evaporate 10% of the liquid, might be substituted for the superheater. The lower temperatures which could be used with such a unit would permit the juice to be heated longer without alteration of the flavor and also permit the use of lower pressure steam for the heating medium. The use of this type of vaporization is under investigation.

Numerous designs are available for vapor-liquid separators. For most efficient separation of vapor and liquid, the flashing should not take place at the entrance to the separating chamber but in a tube leading to it and connected to it tangentially. In this way use is made of the high velocity of the flashed liquid-vapor mixture for separating the liquid from the vapor by centrifugal action.

The fractionating column can be constructed from a single piece of large-diameter pipe and filled with suitable packing material, such as ceramic Raschig rings. The pilot plant studies showed that a column packed to a height of $3\frac{1}{2}$ feet is sufficient if cold reflux is used. If the reflux is returned hot, a taller column may be required. In any event, it is customary to increase the height somewhat when the diameter of a packed column is increased in order to allow for non-uniformity of flow of reflux down the column. Provision must be made for maintaining a small reboiler (coiled, steam-heated tube) immersed in liquid at the base. The amount of reboiling required to prevent loss of flavor in the bottoms product from the column could be reduced by the addition of a length of packed column below the vapor-feed

inlet, which would function as a stripping section. It is doubtful, however, whether the saving in heat thus obtained would be significant. The column should be lagged to prevent excessive loss of heat from it.

The condenser should be designed to condense the vapors and then cool the condensate to 70° F. ± 10° F. If cooling water is not available at a low enough temperature, a refrigerated cooler could be placed in series with the condenser to achieve the last few degrees of cooling. In this case better heat economy would be obtained by returning the reflux at whatever temperature it comes from the condenser and using the refrigerated cooler to cool only that portion of the condensate withdrawn as product. For such an arrangement, the vent for non-condensable gases should be located after the liquid cooler but before the product pump.

The product at 70° F. is nearly saturated with volatile flavors. It should therefore be discharged into cooled receivers to avoid loss. After the receiver is filled and tightly capped, it can be stored at room temperature. It would seem to be a desirable precaution, however, to cool the product before it is used.

The cost of producing volatile apple flavor concentrated one-hundred times (that is, 1 gallon of such product per 100 gallons of juice processed) is estimated to be 30 cents per gallon, not including the cost of the juice or the wages of the operator. This is based on a plant processing 5,000 gallons of juice per 24-hour day and operating continuously for a season of 100 days. It is estimated that in such a plant the operator's wages (one man per shift) would add 60 cents per gallon to the cost of the product and that the investment in new equipment for recovery of flavor would be about $3,500.

It is probable that other processors of apple juice, such as vinegar manufacturers, will want to avail themselves of this means of recovering a valuable product, which is now wasted. The cost of adding the flavor-recovery process to different plants will vary. Each prospective manufacturer's case must therefore be considered individually.

INDUSTRIAL APPLICATIONS

One of the most obvious uses of a natural apple flavor is in the manufacture of a concentrated juice from which a full-flavored, natural apple juice can be reconstituted by the addition of water. Such a product can be made by adding the recovered concentrated flavor to a suitable commercial apple juice concentrate; it is indistinguishable by taste and bouquet from the juice freshly pressed from the apples. An apple juice concentrate into which natural apple flavor has been incorporated also has obvious applications in the preparation of sherbets, ices, and fruit jellies.

An apple flavor would also find application in the preparation of table and coating sirups by incorporating the concentrated flavor, for example, in bland apple sirups or other sugar sirups. Other applications will undoubtedly occur to persons in the food industry. For certain uses, a slightly modified apple flavor may be preferable. A "baked apple" flavor is easily obtained by prolonging the heating of the juice prior to flavor recovery.

Since much of the apple juice evaporated commercially goes into products where natural apple flavor is of no value, the volatile flavoring constituents now discarded in the preparation of these products could by this new process be obtained in concentrated form and sold as natural flavoring essence. The principles of this new process should also be applicable to the recovery of natural flavors from berries and other fruits.